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Physical and electrochemical properties of a room temperature molten salt: 1-ethyl-2,3-dimethylimidazolium fluorohydrogenate

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A new room temperature molten salt (room temperature ionic liquid), 1-ethyl-2,3-dimethylimidazolium fluorohydrogenate ($\text{EDMIm}(\text{HF})_{2.3}\text{F}$), has been prepared by the reaction of EDMImCl and large excess of anhydrous hydrogen fluoride (aHF). $\text{EDMIm}(\text{HF})_{2.3}\text{F}$ is composed of EDMIm cation and $(\text{HF})_n\text{F}$ anions (fluorohydrogenate anions) and exhibits the conductivity of 56.9 mS cm^{-1} and viscosity of 6.8 cP at 298 K . Electrochemical window of $\text{EDMIm}(\text{HF})_{2.3}\text{F}$ determined by cyclic voltammetry using a glassy carbon electrode as a working electrode is about 2.9 V that is close to the window of 1-ethyl-3-methylimidazolium fluorohydrogenate ($\text{EMIm}(\text{HF})_{2.3}\text{F}$) reported previously.

Key Words : Room temperature molten salt, Ionic liquid, 2-Methylimidazolium, Electrochemical stability

1 Introduction

Room temperature molten salts (often called room temperature ionic liquid) have some unique properties such as nonvolatility, nonflammability and wide liquid-state temperature range. Applications of room temperature molten salts to electrochemical devices have been studied by many groups, as well as reaction media and catalysts in organic syntheses.^{1 - 3)} Application of room temperature molten salts as electrolytes includes electrical double layer capacitor,^{4, 5)} fuel cell,^{6 - 8)} lithium battery^{9 - 12)} and solar cell.^{13 - 15)} Properties such as high conductivity and wide electrochemical window are preferable for these applications.

Room temperature molten salts containing fluoroanions are now widely studied because of their high stabilities in air.^{1 - 3)} The first vacuum-stable room temperature molten fluorohydrogenate, 1-ethyl-3-methylimidazolium fluorohydrogenate (EMIm(HF)_{2.3}F), was reported in 1999 (Fig. 1).¹⁶⁾ After the report, a series of fluorohydrogenate salts using alkyimidazolium, alkylpyridinium, alkylpyrrolidinium and alkylpiperidinium cations were prepared and characterized.^{17 - 20)} Their applications to electrochemical devices were examined as well as to organic syntheses.^{4, 8, 21 - 24)} They exhibit the same vacuum-stable HF composition, (cation)⁺(HF)_{2.3}F⁻, anionic species identified being (HF)₂F⁻ and (HF)₃F⁻.^{19, 22)} These two fluorohydrogenate anions exchange HF with each other. The prominent property of the series of fluorohydrogenate salts is their high conductivities induced by their low viscosities. Results of Walden's plots and pulsed-gradient spin-echo (PGSE) NMR suggested that no special conduction mechanism such as ion hopping exist in the systems.^{18, 20)}

Electrochemical stability is one of the most important factors of electrolytes for electrochemical devices. There are some reports that alkylation of the 2-position of 1,3-

dialkylimidazolium cation increases the electrochemical stability of the imidazolium cation.¹⁵⁾ In the present study, physical and electrochemical properties of the fluorohydrogenate salt of 1-ethyl-2,3-dimethylimidazolium cation (EDMIm⁺) shown in Fig. 1 was investigated and compared with those of the other fluorohydrogenates reported previously.

2 Experimental

EDMImCl was prepared by the reaction of ethyl chloride (Wako Pure Chemical Industries, purity > 99 %) and the mixture of 1,2-dimethylimidazole (Aldrich, purity 98 %) and acetonitrile dehydrated (Wako Pure Chemical Industries, purity > 99 %) at 373 K for one night in a sealed screw top pressure tube (Ace Glass). The obtained DMImCl was recrystallized several times from acetonitrile solution using ethyl acetate dehydrated (Wako Pure Chemical Industries, purity > 99 %) and dried at 373 K for one week under reduced pressure (~1 Pa). DMIm(HF)_nF was prepared by the reaction of DMImCl and anhydrous hydrogen fluoride (aHF, Daikin Industries, purity > 99 %) dried over K₂NiF₆ (Ozark Mahoning) in a reaction tube made of tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA). Elimination of the volatile gases and addition of fresh HF were repeated several times for complete elimination of chloride in the form of hydrogen chloride. Finally, volatile gases were eliminated by pumping (~1 Pa).

Electrochemical and physical properties were measured in the same manner as reported previously.^{19, 25)}

3 Results and Discussion

According to the elemental analysis, the fluorohydrogenate salt obtained by the reaction of EDMImCl and aHF exhibits the vacuum-stable composition of EDMIm(HF)_{2.3}F at room temperature which is the same as that obtained for the other room temperature molten fluorohydrogenates.¹⁶⁻¹⁹⁾ Comparison of the IR spectrum of EDMIm(HF)_{2.3}F with those obtained for the other fluorodhydrogenates (M⁺(HF)_nF, M = alkali metal and alkylammonium) indicates that EDMIm(HF)_{2.3}F is composed of EDMIm⁺, (HF)₂F⁻ and (HF)₃F.^{18, 19, 21)} Table 1 shows physical properties of EDMIm(HF)_{2.3}F compared with that of EMIm(HF)_{2.3}F.¹⁸⁾ Figure 2 shows the DSC thermogram of EDMIm(HF)_{2.3}F. EDMIm(HF)_{2.3}F freezes at about 200 K in the cooling process. In the heating process, two melting points at 215 and 237 K were observed, presumably corresponding to the crystallization of EDMIm(HF)₂F and to EDMIm(HF)₃F, respectively.

Figure 3 shows Arrhenius plots of the conductivity and viscosity of EDMIm(HF)_{2.3}F. The conductivity and viscosity of EDMIm(HF)_{2.3}F exhibit almost linear response in the measured temperature range. The conductivity of EDMIm(HF)_{2.3}F at 298 K is 56.9 mS cm⁻¹. This value is much higher than those of the other room temperature molten salts such as 13.6 mS cm⁻¹ of EMImBF₄ and 8.8 mS cm⁻¹ of EMImN(SO₂CF₃)₂.^{15, 26)} The viscosity of EDMIm(HF)_{2.3}F at 298 K is 6.8 cP which is also much lower than those of the other room temperature molten salts such as 31.8 cP of EMImBF₄ and 34 cP of EMImN(SO₂CF₃)₂. As described in the previous studies, the low viscosity is one of the prominent characteristics of fluorohydrogenate salts which provides high conductivities to them.^{18, 20)}

Figure 4 shows cyclic voltammograms of glassy carbon electrodes in EDMIm(HF)_{2.3}F and EMIm(HF)_{2.3}F. As mentioned in the introduction part, according to some reports, the alkylation of the 2-position of imidazolium cation improves the electrochemical stability of the salt. The electrochemical window of EDMIm(HF)_{2.3}F is 2.9 V which is close to that of EMIm(HF)_{2.3}F (3 V). It is known that cathode limits of fluorohydrogenate salts involve hydrogen gas evolution from (HF)_nF⁻. In the case of the tetraalkylammonium fluorohydrogenates (R₄N(HF)_nF) of which the *n* is more than 3.0, hydrogen gas easily evolves at the cathode limit, whereas in the case less than 3.0, the reduction of cation is involved.²⁷⁾ On the other hand, cathode-limit potential of EMIm(HF)_nF is not sensitive to *n* in the region of 1 < *n* < 2.3.²⁸⁾ The cathode limit of EDMIm(HF)_{2.3}F is about -1.8 V vs. Fc⁺/Fc and close to that of EMIm(HF)_{2.3}F. Taking account that EMIm cation is reduced at about -2.5 V vs. Fc⁺/Fc¹⁰⁾, hydrogen gas evolution is predominant in the cathode limits of EDMIm(HF)_{2.3}F and EMIm(HF)_{2.3}F. Aromatic compounds such as benzene are electrochemically fluorinated in fluorohydrogenate salts.^{24, 27)} The more negative anode limit of EMIm(HF)_{2.3}F than those of the other EMIm salts such as EMImBF₄ or EMImN(SO₂CF₃)₂ is probably due to the oxidation accompanied by fluorination of EMIm cation under the existence of fluorohydrogenate anion. Potential of the anode limit of EDMIm(HF)_{2.3}F is close to that of EMIm(HF)_{2.3}F, but the current density of the peak at around 1.1 V in the cyclic voltammogram of EDMIm(HF)_{2.3}F is smaller than that of EMIm(HF)_{2.3}F. This observation indicates that the methylation of the 2-position of imidazolium cation suppresses the electrochemical fluorination of the cation.

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Figure captions

Fig. 1 Structures of (a) EMIm⁺, (b) EDMIm⁺, (c) (HF)₂F⁻ and (HF)₃F⁻.

Fig. 2 DSC curve of EDMIm(HF)_{2.3}F. Scan rate was 5 K min⁻¹.

Fig. 3 Arrhenius plots of the viscosity and conductivity of EDMIm(HF)_{2.3}F. ○: viscosity, □: conductivity.

Fig. 4 Comparison of electrochemical windows of (a) EDMIm(HF)_{2.3}F and (b) EMIm(HF)_{2.3}F. W.E.: GC disk, C.E.: Pt plate, Scanning rate: 10 mV s⁻¹. The potential is referenced to the potential of ferrocenium / ferrocene (Fc⁺/Fc) redox couple in each salt.

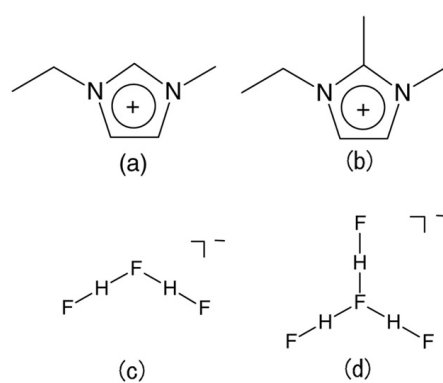


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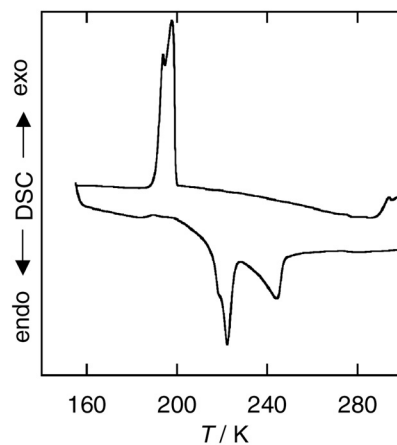


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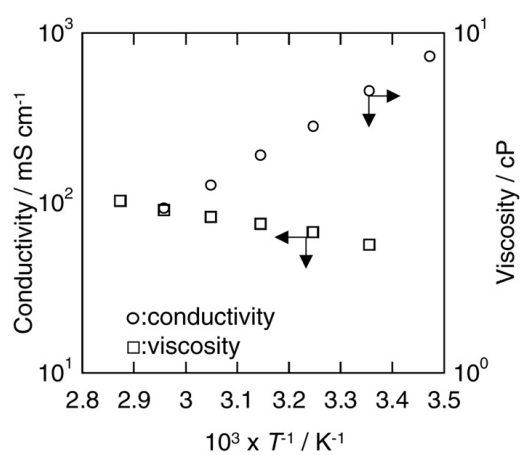


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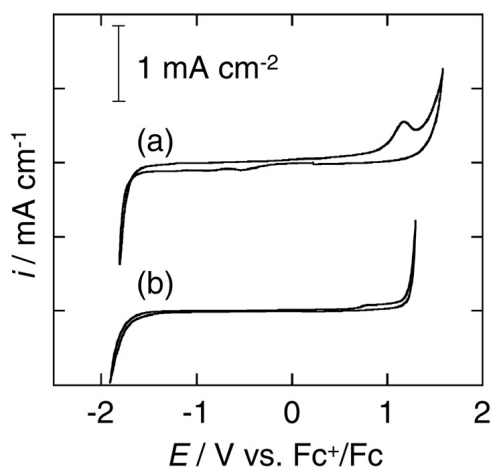


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Table 1 Comparison of physical properties of EDMIm(HF)_{2.3}F and EMIm(HF)_{2.3}F at 298 K.

Salts	M	T_S	T_L	T_g	ρ	η	σ
	W	/K	/K	/K	/ g cm ⁻³	/cP	/ mS cm ⁻¹
EDMIm(HF) _{2.3} F	188	215	237	-	1.10	6.8	56.9
EMIm(HF) _{2.3} F ¹⁸⁾	176	208	208	148	1.13	4.9	100

MW: molecular weight, T_S : solidus temperature, T_L : liquidus temperature, T_g : glass transition temperature, ρ : density, η : viscosity, σ : conductivity.